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Quantitative Speciation of Insoluble Chlorine in Environmental Solid Samples

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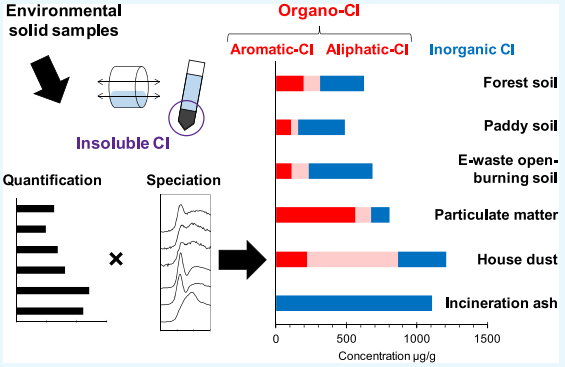
Supporting Information

ABSTRACT: Since organically bound chlorine (organo-Cl) has been determined by different methods depending on samples and study fields, it has been difficult to compare organo-Cl in different environments. Here, we focused on Cl in water-insoluble fractions (insoluble Cl) and applied Cl K-edge X-ray absorption spectroscopy in conjunction with combustion ion chromatography. Quantitative speciation of insoluble Cl enabled us to compare the concentrations of Cl bonded with aromatic carbon (aromatic-Cl) and aliphatic carbon (aliphatic-Cl) as well as organo-Cl across different types of environmental solid samples (soils, particulate matter, dust, and ashes). The concentrations of organo-Cl in house dust and urban particulate matter exceeded those in forest soils, suggesting that house dust and urban particulate matter may be important pools of organochlorine compounds (OCs). Further, by studying representative samples with concentrations of some individual organochlorine compounds (OCs), we evaluated the mass balance of identified/unidentified organo-Cl. The percentages of identified Cl to organo-Cl were up to 1% in all samples evaluated, suggesting the ubiquitous presence of unidentified OCs. We also estimated the chemical forms of insoluble inorganic Cl and tested the plots of organo-Cl versus total organic carbon to find the difference between samples. This work shows that the quantitative speciation of insoluble Cl is effective for cross-comparison of organo-Cl in different environmental solid samples.



INTRODUCTION

Several organochlorine compounds (OCs), such as organochlorine pesticides, polychlorinated biphenyls (PCBs), and polychlorinated dibenzo-*p*-dioxins/furans (PCDD/Fs), have drawn much attention as persistent organic pollutants (POPs) due to their persistence, bioaccumulation, and toxicity. These compounds are mainly produced via anthropogenic activities (both intentional and unintentional) and are widely distributed throughout the environment.[1,2] In addition, numerous OCs are also produced naturally by biotic and abiotic processes in the environment.[3−10]

To assess the impact of anthropogenic and natural production of OCs, comparison of organically bound chlorine (organo-Cl) across different environments is essential. However, different methods have been applied to determine organo-Cl in different samples, which made it difficult to compare. Two parameters have mainly been used to estimate the concentrations of organo-Cl in environmental solid samples: extractable organochlorine (EOCl) and total organochlorine (TOCl). They have been measured after chemical treatment to separate organic and inorganic Cl. EOCl comprises Cl extracted by organic solvents, and Cl in extractable fractions, based on the principle that most POP-like OCs are lipophilic.[2] EOCl has been studied in sediments,[11−15] biota,[11,15−21] ash,[22] and atmospheric particulate matter (PM).[23] These studies reported that only 0.4−45% of EOCl is identified. However, EOCl may underestimate concentrations of organo-Cl because not all OCs are extractable via the same extraction method and some are

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Table 1. Concentrations (μg/g) of Total Chlorine, Insoluble Chlorine, Each Chemical Species of Chlorine (Aromatic-Cl, Aliphatic-Cl, Organo-Cl, and Inorganic Cl) in Total Cl and Insoluble Cl, Identified Cl, and Cl in Five Groups of Identified Organochlorine Compounds for Nine Environmental Solid Samples[a]

sample	natural forest soil	forest soil SRM 0−5 cm	forest soil SRM 5−10 cm	paddy soil	E-waste open-burning soil	urban PM	house dust	bottom ash	fly ash
				Concentrations of Cl (μg/g)					
total Cl	740	810	780	1200	3600	4300	10 000	6100	110 000
organo-Cl[b]	590	440	300	<120	<360	930	<1000	<610	<11 000
aromatic-Cl	360	280	200	<120	<360	930	<1000	<610	<11 000
aliphatic-Cl	230	160	100	<120	<360	<430	<1000	<610	<11 000
inorganic Cl	150	370	480	1200	3600	3400	<1000	6100	110 000
insoluble Cl	550	630	620	490	690	800	1200	1400	1100
organo-Cl[b]	320	310	310	160	230	670	870	<140	<110
aromatic-Cl	220	200	190	100	110	560	220	<140	<110
aliphatic-Cl	110	110	120	50	120	110	640	<140	<110
inorganic Cl	230	310	310	330	450	130	340	1400	1100
identified Cl[c]		0.0058	0.0020		0.28	0.61	1.1	0.0048	0.11
PCBs	na	0.0016[d]	0.00063[d]	na	0.073	0.40	0.28	0.00014[d]	0.0020[d]
PCDD/DFs	na	0.0042	0.0014	na	na	na	na	0.0047	0.11
pesticides	na	na	na	na	na	0.21[e]	0.81[f]	na	na
CBzs	na	na	na	na	0.20	0.0039[g]	0.015[h]	na	na
ClPAHs	na	na	na	na	0.0047	na	na	na	na

[a]na: not analyzed [b]Sum of aromatic-Cl and aliphatic-Cl. [c]Calculated from the certified values for SRMs or reported values for E-waste open-burning soil.[50,51] [d]Only dioxin-like PCBs are included. [e]DDTs, CHLs, HCHs, and toxaphene are included. [f]DDTs, CHLs, HCHs, drins, and heptachlors are included. [g]Only hexachlorobenzene is included. [h]Only pentachlorobenzene is included.

nonextractable[14] (see Figure S1). Thus, we need some other methods to evaluate organo-Cl, including nonextractable one.

TOCl is Cl remaining in residues after washing by aqueous solution, or the Cl in insoluble fractions. This method is based on the principle that most inorganic chlorine compounds are water-soluble and most OCs are hydrophobic.[24] TOCl has been quantified in soil,[24−26] humic acid,[27] peat bog,[28] and sediment,[14,29] indicating the ubiquitous existence of naturally produced OCs; however, TOCl may overestimate concentrations of organo-Cl[28] due to the remaining inorganic Cl after washing (Figure S1). Particularly, application of TOCl to samples containing large amounts of insoluble inorganic Cl[30] is difficult. To date, there have been few studies specifying the inorganic Cl remaining after washing.

Cl K-edge X-ray absorption near-edge structure (XANES) is an effective technique for determining the chemical forms of Cl, especially inorganic Cl, Cl bonded with aromatic carbon (aromatic-Cl), and Cl bonded with aliphatic carbon (aliphatic-Cl) individually.[8,10,31−34] Myneni[8] showed that inorganic Cl is dominant in living plant tissues, but it is converted into organo-Cl (dominated by aromatic-Cl) during humification. Fujimori and Takaoka[31] demonstrated the reaction between inorganic Cl and organo-Cl during the thermal process by measuring in situ Cl XANES during model fly ash heating. Leri et al. studied the analytical procedure for accurate quantitative speciation of Cl.[32] The problem of this technique is that we cannot distinguish very small proportion (less than 10%) of organo-Cl. Therefore, combination of this Cl K-edge XANES technique and chemical treatment used for TOCl or EOCl analyses is expected to contribute to more accurate determination of organo-Cl in insoluble or extractable fractions. Particularly, quantitative speciation of insoluble Cl is promising because XANES technique is more suitable for the analysis of solid samples.[33,34] For instance, Leri et al. measured sediment samples after rinsing.[34]

Determination of organo-Cl in conjunction with the analysis of individual OCs could afford a better understanding of the presence and distribution of unidentified OCs,[11−23] which can lead to assess potential environmental pollution and to motivate studies for identifying the unsuspected persistent OCs. Standard reference materials (SRMs) with certified concentrations of OCs are promising samples because the concentrations of some OCs are known and are available to all researchers.

In this study, we performed the quantitative speciation of insoluble Cl. We adopted the method to representative solid samples from various solid phases: forest soils, rice field paddy soil, electronic waste (E-waste) open-burning soil, urban PM, house dust, municipal solid waste incineration (MSWI) fly ash, and MSWI bottom ash. Since these solid samples act as sources, stores, and sinks of OCs in the environment,[35−39] potentials of OCs in them are of interest. The concentrations of aromatic-Cl and aliphatic-Cl as well as organo-Cl were evaluated to compare the potentials of OCs among the samples, and to identify candidates that have high potentials of OCs. Furthermore, by choosing samples with certified or reported concentrations of individual OCs, the mass balance of identified/unidentified organo-Cl was studied. We also showed the estimated chemical forms of inorganic Cl in insoluble Cl. Finally, we characterized organo-Cl in different samples using the relationship between organo-Cl and total organic carbon (TOC).

RESULTS AND DISCUSSION

Total Chlorine (TCl) and Insoluble Cl. Concentrations of total chlorine (TCl) and insoluble chlorine (insoluble Cl) are shown in Table 1 and Figure 1. TCl concentrations varied greatly, with differences in the range of 3 orders of magnitude (740−110 000 μg/g); concentrations of insoluble Cl showed smaller differences (490−1400 μg/g). The percentage of insoluble Cl contained in TCl was 74−79% in forest soils

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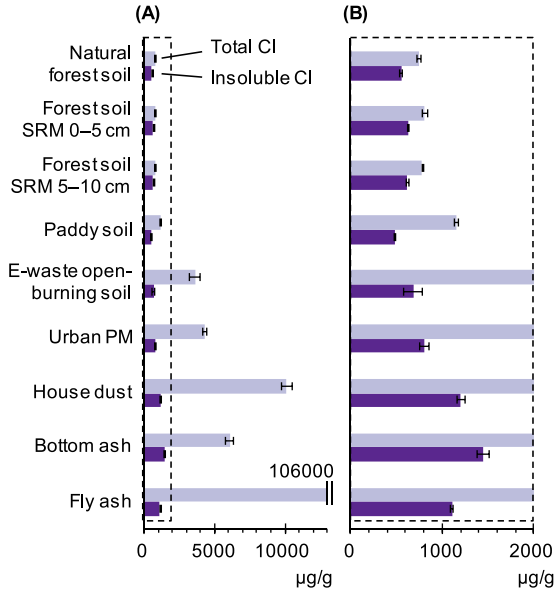

Figure 1. (A) Concentrations of total chlorine (TCl) and insoluble chlorine (insoluble Cl) in each sample measured by combustion ion chromatography. (B) Enlarged view of a part encircled by a dotted line in (A).

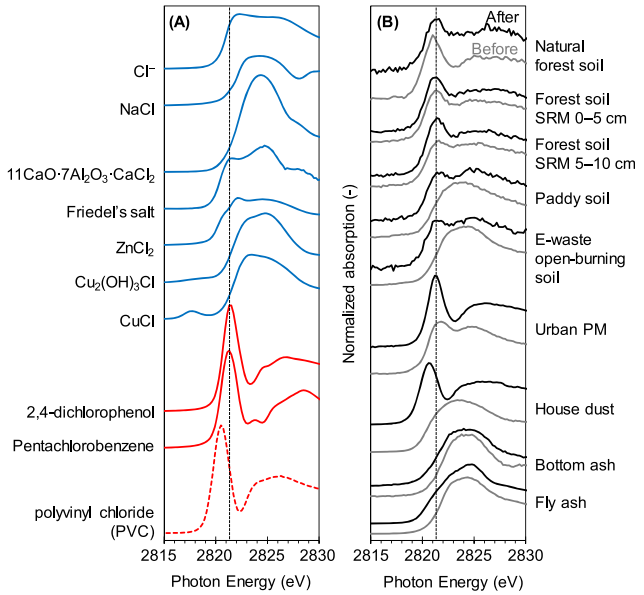

Figure 2. (A) Cl K-edge X-ray absorption near-edge structure (XANES) spectra of standard compounds finally fitted to any of sample spectra in the linear combination fitting (LCF) analysis. The blue solid lines indicate the spectra of inorganic Cl compounds, the red solid lines indicate the spectra of aromatic-Cl compounds, and the red dotted line indicates the spectrum of an aliphatic-Cl compound. (B) Cl K-edge XANES spectra of the samples. The black spectra (top panel) are those after washing; the gray spectra (bottom panel) are those before washing. The vertical line at 2821.1 eV indicates the peak position of aromatic-Cl.

(natural forest soil, forest soil SRM 0–5 cm, and forest soil SRM 5–10 cm), 42% in paddy soils, 19% in E-waste open-burning soil and in urban PM, 12% in house dust, 24% in bottom ash, and 1% in fly ash. These results indicate that the water-soluble fraction, mainly consisting of inorganic salts, differed among samples and was representative of the general features of each sample.

TCl concentration observed in urban PM (4300 ± 160 μg/g) was similar to the certified value (4543 ± 47 μg/g). Based on this, we conclude that our results are reliable. The concentrations of TCl observed in forest soils in this study were comparable to previously reported values, i.e., in the range of 25–1040 μg/g (45–1040 μg/g for humus and 25–210 μg/g for mineral soils), as measured by instrumental neutron activation analysis for 51 French forest soils collected from various forest types and climates.[26] Insoluble Cl is also reported to represent approximately 60–80% of the total Cl in previous reports about forest soils;[26,40] this range is similar to that observed in forest soils in our study (74–79%). Paddy soil TCl (1200 ± 20 μg/g) was higher than the concentrations reported previously for agricultural soils (19–100 μg/g), and the ratio of insoluble Cl to TCl was 2-fold lower than that previously reported.[25] This difference might be due to differences in the crops planted or soil type. Similar concentrations of TCl in fly ash and bottom ash have been reported previously.[41,42]

Cl K-Edge XANES Spectra before and after Washing. The Cl K-edge XANES spectra of standard chemicals are presented in Figures 2A and S2. The maximum peaks of inorganic Cl, aromatic-Cl, and aliphatic-Cl occurred at 2822–2825, 2821.2 ± 0.1, and 2820.5 eV, respectively (Figures 2A and S2). Compared with inorganic Cl, C–Cl bonds exhibited a peak that is 1–4 eV lower. The peaks of aliphatic-Cl occurred at 0.7 eV lower than aromatic-Cl. These were consistent with previous reports.[8,10,34,43] As shown in Figure 2A, differences in the shape of the spectra between 2815 and 2830 eV were large enough to distinguish between aromatic-Cl, aliphatic-Cl, and different species of inorganic Cl.

The Cl K-edge XANES spectra of samples before and after washing are shown in Figure 2B. On comparing the spectra before and after washing, clear changes were observed in house dust, E-waste open-burning soil, and paddy soil. Before washing, the peak was in the range of 2823–2825 eV, indicating that inorganic Cl was dominant; however, after washing, peaks at 2820.8–2821.5 eV were observed, indicating that organo-Cl became dominant (see Figure 3). These results suggest that most of the inorganic Cl was removed by washing.

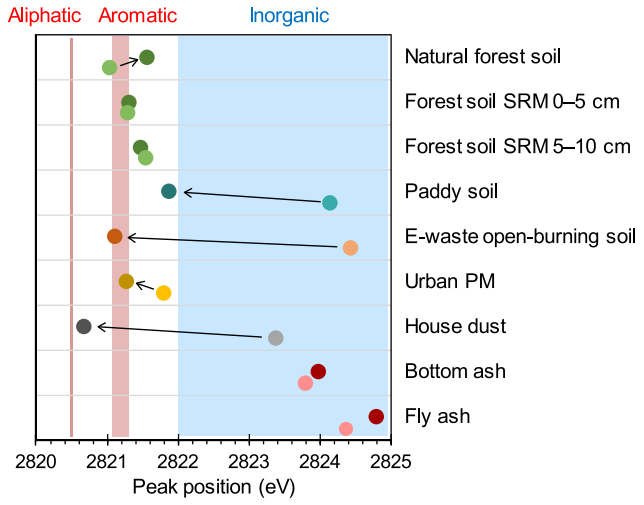

Figure 3. Peak position (eV) of samples before (light colored) and after washing (dark colored).

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By taking a closer look at the peak position after washing, we could assess the chemical species (Figures 2B and 3).

House dust after washing showed a sharp peak at 2820.7 eV, indicating that aliphatic-Cl was dominant. E-waste open-burning soil and paddy soil showed a small peak at 2821−2822 eV, indicating that aromatic-Cl is higher than aliphatic-Cl and considerable portions of inorganic Cl species are still present. In urban PM, a small peak at 2821.5 eV was observed before washing, indicating that comparable proportions of organo-Cl (mainly aromatic-Cl) and inorganic Cl coexisted before washing. Huggins et al.[44] reported the Cl XANES spectra of NIST SRM 1648 (the older batch of SRM used in this study; SRM 1648a), which was consistent with our result. Urban PM after washing showed one sharp peak at 2821.2 eV, indicating that inorganic Cl decreased and organo-Cl (mainly aromatic-Cl) became dominant. The shift of the peak position to lower energy (2821.5−2821 eV) can be explained by the peak position possibly being affected by inorganic Cl before washing (Figure 3).

The spectra were similar between natural forest soil and soil SRMs; peaks occurred at 2821−2821.5 eV both before and after washing, indicating that organo-Cl (mainly aromatic-Cl) is dominant in forest soils. Small differences were observed in the spectra of these samples before and after washing. In natural forest soil, the peak was smaller after washing (Figure 2B) and the peak position shifted to the higher energy (Figure 3), suggesting that some organo-Cl was washed out. In the forest soil SRM 0−5 cm, the peak became broader (Figure 2B) and the peak position also shifted to the higher energy (Figure 3), indicating a decrease in the proportion of organo-Cl, also suggesting the water-soluble organo-Cl. In the forest soil SRM 5−10 cm, the peak became sharper after washing (Figure 2B) and the peak position shifted to lower energy (Figure 3), indicating that inorganic Cl was removed. Possible existence of water-soluble organo-Cl will be discussed further in the quantitative speciation part.

Fly ash and bottom ash showed peaks at 2823.5−2825 eV both before and after washing (Figures 2B and 3), suggesting that inorganic Cl was dominant before washing and remained dominant after washing. Zhu et al.[30] combined XANES and X-ray diffraction (XRD) analysis to determine the chemical forms of Cl and its proportion. They reported that 13% of Cl was $[Ca_2Al(OH)_6]Cl{\cdot}2H_2O$ (insoluble Cl salt, known as Friedel's salt) in fly ash collected in a bag filter with the injection of calcium hydroxide for acid gas removal (i.e., similar fly ash to that used in this study), suggesting that the insoluble Cl salt concentration is so high that organo-Cl is unlikely to be a major component even after washing. The result for bottom ash was likely caused by a similar phenomenon. Chemical forms of insoluble inorganic Cl will be discussed later.

Cl Speciation before and after Washing. The linear combination fitting (LCF) results before and after washing are illustrated in Figure 4. In forest soils, aromatic-Cl and aliphatic-Cl were more than 10% before washing as Myneni reported,[11] suggesting that washing is unnecessary for forest soils when measuring quantitative speciation using XANES.

Except for forest soils (natural forest soil and forest soil SRMs), the proportions of aromatic-Cl and/or aliphatic-Cl were below 10% before washing. After washing, the proportions of aromatic-Cl and aliphatic-Cl were significantly increased in house dust, urban PM, E-waste open-burning soil, and paddy soil (Figure 4). This is consistent with the clear shifts in spectral shapes and peak positions (see Figures 2B and 3), showing the effectiveness of washing for precise estimation of aromatic-Cl and aliphatic-Cl. Although we were unable to wash out inorganic Cl completely, the percentages of inorganic Cl in these samples after washing were sufficiently small for reliable evaluation of aromatic-Cl and aliphatic-Cl.

In ash samples, however, aromatic-Cl and aliphatic-Cl were still less than 10% after washing. This might be due to the large amounts of inorganic Cl remained even after washing. More inorganic Cl should be removed to obtain reliable fitting results

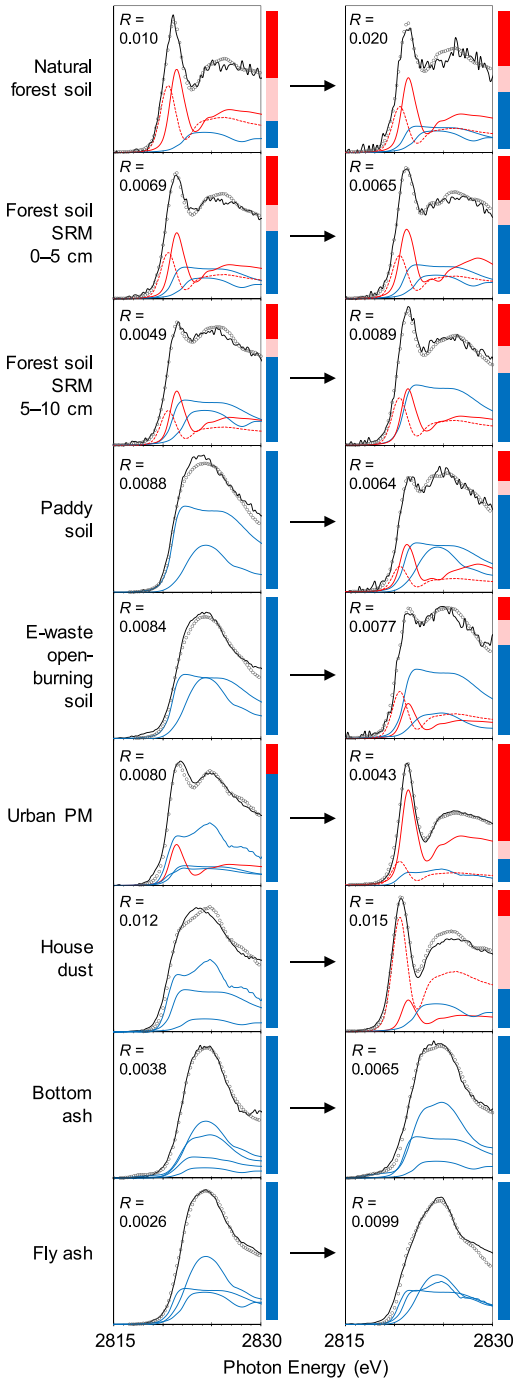

Figure 4. Cl K-edge XANES spectra of samples (black solid lines) and the best fit (circles) calculated from the standard spectra (colored spectra, also shown in Figure 2). *R* values for each fit are given in the top left position of each graph. The bars to the right denote the proportions of aromatic-Cl (red areas), aliphatic-Cl (pink areas), and inorganic Cl (blue areas). The arrows indicate washing.

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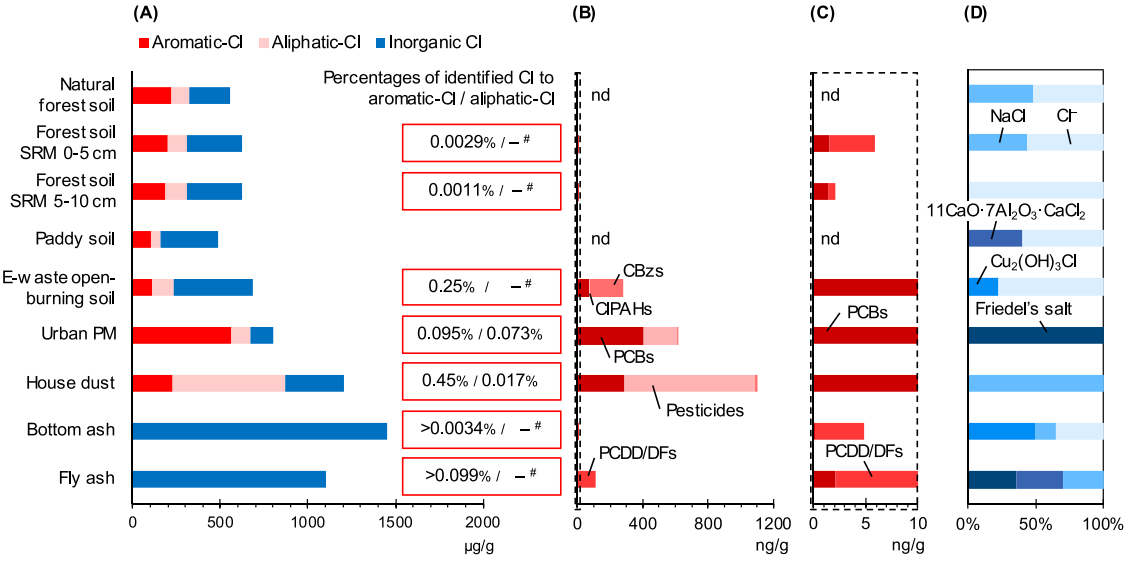

Figure 5. (A) Estimated concentrations of aromatic-Cl, aliphatic-Cl, and inorganic Cl in insoluble Cl. (B) Concentrations of Cl in each identified organochlorine compound; nd, no certified or reported data for identified compounds. (C) Enlarged view of a part encircled by a dotted line in (B). (D) Estimated proportions of chemical forms of insoluble inorganic Cl. # No identified compound contained aliphatic-Cl.

for aromatic-Cl and aliphatic-Cl. For instance, CO_2 bubbling and pH adjustment are promising techniques to remove insoluble Cl.[45,46] XRD analysis and XANES technique can be used for knowing whether insoluble Cl was removed or not.

Quantitative Speciation of Insoluble Cl. By multiplying the concentrations of Cl and proportions of chemical species, the concentrations of each chemical species were estimated, i.e., quantitative speciation was performed. Figure S3 shows the quantitative speciation before and after washing. The estimated concentration of organo-Cl decreased in some samples, i.e., by 45% in natural forest soil, 29% in the 0−5 cm forest soil SRM, and 27% in urban PM after washing (Table 1). This result may have occurred because some organo-Cl is soluble and thus removed by washing. Leri and Myneni[33] reported that soluble aromatic-Cl was present in tree leaves and leached into the soil during the first stage of degradation. With respect to urban PM, organo-Cl decreased by 27%. Zappoli et al.[47] reported that about 50% of organic carbon in aerosols is water-soluble; some OCs may have similar properties. Because of the possible presence of water-soluble organo-Cl, washing is obviously a crucial step for the evaluation of aromatic-Cl and aliphatic-Cl in some samples. And our original target in this study was POP-like OCs, which are relatively insoluble to aqueous solutions. Therefore, we mainly discuss quantitative speciation of insoluble Cl below.

Figure 5A shows the quantitative speciation of insoluble Cl. Concentrations of each chemical species showed various unique characteristics of each sample. In forest soils, aromatic-Cl was abundant. The concentration of aromatic-Cl was 1.5−2.1 times higher than that of aliphatic-Cl, which is consistent with previous reports.[8,10,33] Two forest soil SRMs from different depths showed similar concentrations of both aromatic-Cl and aliphatic-Cl. A clear difference between forest soil SRMs (collected near MSWI plant) and natural forest soil sample was not observed. These results suggest that the impact of the MSWI plant, a local source of pollution to organo-Cl, is negligible. Paddy soil showed smaller concentrations of aromatic-Cl and aliphatic-Cl than those of forest soils, indicating that this paddy soil is a more mineralized one.

In the E-waste open-burning soil, organo-Cl concentration (230 μg/g) was lower than that in forest soils (average, 310 μg/g), although considerable amounts of organo-Cl are expected to be generated by E-waste burning activity in addition to known individual OCs.[48−51] As far as our samples are concerned, it is assumed that naturally produced organo-Cl in forest soils is higher than organo-Cl generated by E-waste open-burning activity. Focusing on the chemical species (aromatic-Cl vs aliphatic-Cl), aliphatic-Cl was a little higher than aromatic-Cl in E-waste open-burning soil, while aromatic-Cl was 1.8 times higher than that of aliphatic-Cl in forest soils. This is likely due to the presence of poly(vinyl chloride) (PVC) and its decomposed compounds. PVC is commonly used to coat wires and cables, and thus is a major component of E-waste. Fujimori et al.[49] suggested that PVC interacts thermochemically with copper to promote the formation of dioxin-related compounds during E-waste open burning.

In urban PM, the organo-Cl concentration was more than twice higher (670 μg/g) than forest soils (average, 310 μg/g) and the aromatic-Cl concentration was highest (560 μg/g) among the samples in this study. Aliphatic-Cl concentration in urban PM was not significantly high (110 μg/g), although hydrocarbon and its related compounds account for a significant proportion of all aerosols[52] and large amounts of halocarbons are released into the atmosphere.[53] One possible source is anthropogenic release. Many semivolatile organic compounds, including aromatic OCs, such as PCDD/Fs,[54] PCBs,[55] chlorinated pesticides,[56] and chlorinated polycyclic aromatic hydrocarbons (ClPAHs),[57] are ubiquitous in the atmosphere. Another possibility is natural chlorination of organic compounds.[58] Zappoli et al.[47] reported the abundance of water-insoluble organic carbon of 0.1−3.5 μg/m^3 or 20−144 μg/g. It is possible to assume that insoluble organic carbon may be chlorinated naturally. Participation of soil particle from dust storms[59] is also considered from the result that aromatic-Cl is more abundant than aliphatic-Cl. Further studies about organo-Cl in atmospheric environment are expected.

In house dust, the aliphatic-Cl was dominant (53%) and the concentration was highest (640 μg/g) among the samples in

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this study. This may originate from fibers, where one of the major components of house dust is fibers including lint from clothing; some of these fibers are made of aliphatic-Cl (e.g., PVC). Certain aliphatic compounds, like chlorinated paraffins (CPs),[60] may also be abundant. Aromatic-Cl content (220 μg/g) was comparable to that of forest soils, suggesting that aromatic-Cl is also abundant in the indoor environment.

In ash samples, we were unable to estimate organo-Cl because they are less than 10% of insoluble Cl. Matsui et al.[22] reported EOCl concentrations of 4.98−24.17 and 2.75−17.73 μg/g in fly ash and bottom ash, respectively. These values represent about 0.2−2% of the insoluble Cl detected in this study, indicating that organo-Cl is negligible in insoluble fractions.

From the comparison of organo-Cl in each sample (Table 1 and Figure 5A), we found that concentrations of organo-Cl in house dust and urban PM exceeded the concentrations of organo-Cl in forest soils. This suggests the possibility that house dust and urban PM are large pools as well as forest soil, a notable pool of organo-Cl. Focusing on the chemical forms, aliphatic-Cl was remarkable in house dust and aromatic-Cl was significant in urban PM. Paddy soil, which has poor organic compounds, showed lower concentration of organo-Cl compared to forest soils with similar composition of aromatic-Cl and aliphatic-Cl. E-waste open-burning soil showed lower concentration of organo-Cl than forest soil, but the presence of OCs related to combusted residue was suggested from the composition of aromatic-Cl and aliphatic-Cl. For ash samples, we could not estimate organo-Cl concentrations, but they are expected to be lower than other samples.

Insoluble Organo-Cl versus Identified Cl. Based on the contribution of identified Cl, we determined that more than 99% of organo-Cl was unidentified in all samples capable of being evaluated (Table 1 and Figure 5A−C). In forest soil SRMs, known compounds (12 dioxin-like PCB congeners and PCDD/DFs) contributed less than 0.003% of the Cl to aromatic-Cl (Table 1 and Figure 5A−C), which was smaller than the amount that they contributed to other samples; this suggests the abundance of naturally produced OCs in forest soils.

In urban PM, 58 PCB congeners and 34 chlorinated pesticides contributed 0.095% of the Cl to aromatic-Cl and 0.073% to aliphatic-Cl (Table 1 and Figure 5A−C). This is consistent with the previous report that known OCs (chlorinated pesticides and PCBs) accounted for 0.04−0.7 and 0.06−0.3% of EOCl in PM2.5 and PM10, respectively.[23] The identified Cl contribution of OCs to urban PM was 33−86 times higher than that to forest soil SRMs, indicating that the impacts of the identified compounds were larger in urban PM than those in forest soil.

In house dust, 58 PCB congeners and 34 chlorinated pesticides contributed 0.45% of the Cl to aromatic-Cl and 0.017% to aliphatic-Cl (Table 1 and Figure 5A−C); these contributions were larger than those for soils and urban PM. For comparison, we also investigated the Cl contribution of PCBs alone, which was the largest among those for other samples in this study (Figure 5B,C), suggesting that house dust is a notable sink of POP-like OCs. Further, we roughly estimated the Cl contributions of CPs (known as POP-like aliphatic OCs) using the CP values reported previously for a sample SRM 2585 (the same SRM used in our study),[61,62] assuming that the total concentration of short-chain CPs (C10−13) was 7 μg/g, with an average Cl content of 60% (mass basis), and that the total concentration of medium-chain CPs (C14−17) was 16 μg/g, with an average Cl content of 45% (mass basis). According to this estimation, at least 10 μg/g of Cl was derived from CPs, which are expected to contribute about 1.5% to aliphatic-Cl in this study. It is assumed that similar chlorinated alkanes are present in large concentrations within house dust.

For E-waste open-burning soil, Ito et al.[50] and Nishimura et al.[51] compared concentrations of PCBs, polychlorinated benzenes (CBzs), and ClPAHs in samples collected from the same area (N5°33′, W0°13′) within the same period (August 2013). We calculated the Cl contributions of PCBs, CBzs, and ClPAHs to aromatic-Cl and found that the total Cl contribution was 0.25%. Large amounts of other OCs may be produced along similar pathways to the identified OCs during E-waste open burning.

The results suggest the anthropogenic and natural release of unidentified OCs in various environments. In E-waste open-burning soil, urban PM, and house dust, a similar trend was observed for Cl in PCBs and aromatic-Cl. This indicates that unidentified OCs in these three samples may have similar physicochemical properties to PCBs. In forest soils, organo-Cl was higher than E-waste open-burning soil and comparable to house dust, although quite low concentrations of Cl were explained by PCBs and PCDD/DFs. This indicates the abundance of OCs that have different characteristics from POP-like compounds like PCBs and PCDD/DFs.

Chemical Forms of Insoluble Inorganic Cl. According to the LCF results, insoluble inorganic Cl was present in all samples (Figure 5A and Table S5). Thus, we investigated the contributions (%) of each chemical form of Cl to the insoluble inorganic Cl. The contributions varied among the samples (Figure 5D and Table S5).

Chloride ion (Cl^-) was observed in all soil samples and bottom ash; therefore, Cl^- remained despite the expectation that it would be dissolved and removed by washing. One possibility for this result is that Cl^- is adsorbed on the surface of the solid phase.[63]

NaCl was observed in natural forest soil, forest soil SRM 0−5 cm, ash samples, and house dust. These results suggest that NaCl or similar compounds may present in an insoluble state in the surface soils and ash. NaCl in house dust may reflect the human activities.

Zhu et al.[30] reported the presence of insoluble Cl in waste incineration fly ash; it is therefore reasonable to use Friedel's salt (i.e., $[Ca_2Al(OH)_6]Cl{\cdot}2H_2O$) and its related compounds (e.g., $11CaO{\cdot}7Al_2O_3{\cdot}CaCl_2$) as standards for insoluble Cl in fly ash. In the current study, 36% of the inorganic Cl observed in fly ash after washing was Friedel's salt and 34% was $11CaO{\cdot}7Al_2O_3{\cdot}CaCl_2$. This result can be explained by reports showing that $11CaO{\cdot}7Al_2O_3{\cdot}CaCl_2$ is formed when Friedel's salt is heated between 290 and 670 °C[64] and can return to Friedel's salt form when placed in water.[65]

Friedel's salt was also observed in urban PM after washing. The presence of similar compounds (which have similar XANES spectra) is expected. This is consistent with the abundance of aluminum (certified concentration, 3.43%) and calcium (certified concentration, 5.84%) in NIST SRM 1648a.

$Cu_2(OH)_3Cl$ was observed in E-waste open-burning soil and bottom ash. This is not strange considering the copper concentrations of these samples: 22 000 mg/kg at maximum for E-waste open-burning soils collected from the same

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ACS Omega 2019, 4, 6126−6137

sampling site[49] and 4990 mg/kg for the same bottom ash (JSAC 0512).[66] Our results are also consistent with the report that $Cu_2(OH)_3Cl$ is one of the major chemical forms of Cl in E-waste open-burning soils[67] and copper chloride hydroxide is one of the major chemical forms of copper in MSWI ash.[41]

Five types of insoluble inorganic Cl compounds are expected to remain after washing in the samples at different compositions. Studies using another technique (e.g., XRD) are expected to further elaborate on inorganic Cl species in the future.

Insoluble Organo-Cl to Total Organic Carbon Ratios. Insoluble organo-Cl to TOC ratios, organo-Cl/TOC, was investigated to characterize organo-Cl in samples (Figure 6).

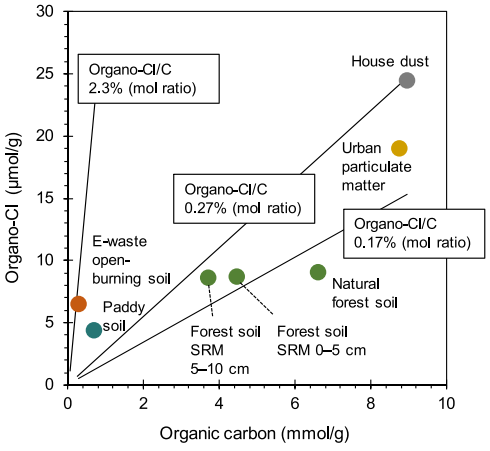

Figure 6. Plots of insoluble organo-Cl (μmol/g) and total organic carbon (TOC) (mmol/g). The slopes of the lines indicate the ratios of organo-Cl to TOC (molar ratio).

TOC concentrations were 7.9% (6.6 mmol/g) in natural forest soil, 5.3% (4.4 mmol/g) in forest soil SRM 0−5 cm, 4.5% (3.7 mmol/g) in forest soil SRM 5−10 cm, 0.84% (0.70 mmol/g) in paddy soil, 0.34% (0.28 mmol/g) in E-waste open-burning soil, 10.8% (9.0 mmol/g) in house dust, 0.6% (0.49 mmol/g) in bottom ash, and 2.3% (1.9 mmol/g) in fly ash. We used the certified value 10.5% (8.7 mmol/g) for urban PM. For ash samples, we could not estimate organo-Cl because they were less than 10% of insoluble Cl. Therefore, we did not include their plots.

Organic carbon is generally considered as a site for the sorption of hydrophobic pollutants.[68] Thus, organo-Cl/TOC may be a good indicator for evaluating how much hydrophobic compounds are included in insoluble organo-Cl. The average organo-Cl/TOC in forest soils was 0.17% (molar ratio), or 5.0 mg Cl/g C, which is of the same order of magnitude as previously reported values.[5,69] Compared to forest soils, organo-Cl/TOC value (indicated by the slopes in Figure 6) was high in house dust (0.27%), paddy soil (0.63%), and E-waste open-burning soil (2.3%). This implies that these samples may include higher content of hydrophobic compounds. On the other hand, urban PM showed similar organo-Cl/TOC value (0.22%) to forest soils. This implies that significant part of organo-Cl in urban PM are expected to be related to less hydrophobic compounds (e.g., humic-like substances[70]). Here, we characterized organo-Cl in different samples using organo-Cl/TOC, but it should be emphasized that not all of the same types of samples (e.g., all of the E-waste open-burning soils) show the same characteristics. Further studies with more data set and statistical analysis are expected.

CONCLUSIONS

Quantitative speciation of insoluble Cl enabled us to compare the concentrations of aromatic-Cl and aliphatic-Cl as well as organo-Cl across different types of solid samples. We revealed that the compositions of aromatic-Cl, aliphatic-Cl, and inorganic Cl in insoluble Cl were characteristic to each sample. Particularly, the concentrations of organo-Cl in house dust and urban PM were found to exceed the concentrations of organo-Cl in forest soils, notable pools of OCs. This suggests that house dust and urban PM may also be important matrices for OCs. Focusing on the chemical speciation, 74% of organo-Cl in house dust was aliphatic-Cl, suggesting the abundance of man-made chlorinated polymers. In urban PM, on the other hand, 84% of organo-Cl was aromatic-Cl. Both natural and anthropogenic sources are expected for this. The presence and probable chemical forms of insoluble inorganic Cl were also investigated by the quantitative speciation of insoluble Cl. The results suggested that insoluble inorganic Cl was also characteristic to each sample and worth studying further in the future. In this study, we used representative samples including SRMs (well composite samples), but they were collected at different locations. Studies about geographic diversity are also expected to be discussed in the future.

From the mass-balance study of identified/unidentified organo-Cl, we revealed that identified Cl accounted up to 1% to organo-Cl evaluated by the quantitative speciation of insoluble Cl. This indicates that large amounts of OCs remain unidentified. The abundance of organo-Cl in natural forest soils suggests that organo-Cl itself does not necessarily show the potential environmental "pollution"; however, it gives us the information about how much unidentified OCs remain unchecked. Further, combination with other techniques can reveal the characteristics of organo-Cl, for instance, the plots of insoluble organo-Cl versus TOC showed the possibility that the E-waste open-burning soil contains high compositions of hydrophobic compounds, which may include unidentified POP-like OCs.

Since SRMs we studied are available to all researchers, our work can be the beginning of the next phase of research (e.g., nontargeted screening analysis) for all of the researchers. Further studies are expected to specify the presence, environmental effects, source, and fate of unidentified OCs in various environments as well as in the forest environment. We are sure that application of the "quantitative speciation of insoluble Cl" is helpful for that.

EXPERIMENTAL SECTION

Materials. We used three field-collected samples and six SRMs in this study: natural forest soil (Mt. Yoshida, Kyoto, Japan),[71] two forest soil SRMs (Japan Society for Analytical Chemistry [JSAC] SRM 0422 [0−5 cm] and 0421 [5−10 cm]), paddy soil (Aomori, Japan),[72] E-waste open-burning soil (Agbogbloshie, Ghana),[48−51,73] urban PM sample (NIST, SRM 1648a), house dust sample (NIST, SRM 2585), MSWI bottom ash (JSAC, SRM 0512), and MSWI fly ash sample (JSAC, SRM 0511). All samples were stored in a refrigerator at 4 °C until analysis. Concentrations of PCBs, PCDD/Fs, and chlorinated pesticides were certified in the SRMs in this study (Tables S1−S3). Detailed information of samples is as below.

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Natural forest soil was collected at Mt. Yoshida, Kyoto, Japan (N35°1′, E135°47′). The soil type was brown forest soil in a warm temperate forest. More detailed information about the site and soil is provided elsewhere.[71] The sample was collected from the A layer (depth: about 5−10 cm) in August 2016 using a spade and transported in polyethylene plastic bags to the laboratory. The sample was then air-dried for 1 week and sieved through 2 mm mesh.

Forest soil SRMs (SRM 0422 and 0421) were obtained from The Japan Society for Analytical Chemistry (JSAC). These samples were collected from a forest neighboring an MSWI plant. Sample 0422 was collected from the surface (0−5 cm depth), and sample 0421 was collected at a depth of 5−10 cm. They were air-dried, sieved through 106 μm mesh, and ball-milled. Concentrations of PCDD/DFs and 12 dioxin-like PCB congeners were measured (Table S1). These samples were considered indicative of a contaminated forest soil compared to the natural forest soil described above.

Paddy soil was collected from a rice paddy field in Aomori Prefecture, Japan, in March 2003. The sample was dried at 50 °C, passed through a 2 mm sieve, and then finely ground with an agate mortar.[71] This sample (No. 2003-5) has been detailed in a previous study.[71]

E-waste open-burning soil was obtained from the Agbogbloshie market, Ghana, in August 2013 (N5°33′, W0°13′). This area is the largest informal E-waste recycling site in Ghana; numerous small E-waste recycling workshops also surround the market. Wires, cables, printed circuit boards, and other materials including plastics are mixed and burned along the edge of the market. Soil samples collected from this area have been examined in previous studies.[48−51,73] A soil/ash mixture sample was collected at a depth of 0−2 cm using a stainless steel auger. The sample was air-dried for 1 week, sieved through 2 mm mesh, and homogenized in the laboratory. PCBs, CBzs, and ClPAHs in samples collected from the same area (N5°33′, W0°13′) within the same period (August 2013) are reported previously.[50,51]

The urban PM sample was obtained from the National Institute of Standards and Technology (NIST, SRM 1648a); it was prepared from urban PM collected in the St. Louis (Missouri) area in a baghouse specially designed for this purpose. The material was collected over a period exceeding 12 months between 1976 and 1977 and subsequently filtered through a 125 μm sieve. Certified or reference values for the 58 PCB congeners and 34 chlorinated pesticides are provided (Table S2). In addition, Cl concentration (4543 ± 47 mg/kg) measured by instrumental neutron activation analysis and organic carbon content (10.5%) measured by thermal-optical organic carbon method are provided as certified and informed values.

The house dust sample came from NIST (SRM 2585); dust was collected from vacuum cleaner bags used in homes, by cleaning services, and in motels and hotels in various U.S. states (North Carolina, Maryland, Ohio, New Jersey, Montana, and Wisconsin) during the period 1993−1994. They were screened through a 90 μm sieve. The concentrations of the 42 PCB congeners and 14 chlorinated pesticides are provided as certified or reference values (Table S3).

The MSWI bottom ash sample was obtained from JSAC sample SRM 0512, and the MSWI fly ash sample was obtained from JSAC SRM 0511. These ash samples were collected from a waste (mainly wood waste) incineration plant in Japan. They were air-dried, sieved through 106 μm mesh, and ball-milled. Concentrations of PCDD/DFs and 12 dioxin-like PCB congeners were certified (Table S1).

Quantification of Insoluble Cl and Total Cl. To prepare insoluble fractions, we applied the following washing pretreatment. First, we mixed 0.1 g of each solid sample with 5 mL of KNO_3 solution (4.1 g/500 mL) and subjected the samples to shaking for 1 h. After the suspension was centrifuged, the residue was washed into another bottle with 10 mL of ultrapure water, shaken for 1 h, and centrifuged. This process (washing into bottle, shaking, and centrifuging) was repeated and the residue was dried in a desiccator (Figure S4). We used this washing method based on preliminary experiments on shaking time and the number of washes (described in Figures S5 and S6). KNO_3 solution was used referring to some previous studies.[9,74,75] We confirmed that the KNO_3 solution does not induce chlorination by comparing Cl concentrations after washing by ultrapure water and KNO_3 solution (Figure S7).

TCl and insoluble Cl were measured by combustion ion chromatography (n = 3).[76] We placed 5 mg of the original sample (for TCl) or residue (for insoluble Cl) on a ceramic boat with 25 mg of WO_3 and then put it into a combustion unit (AQF-2100H; Mitsubishi Chemical Analytech), where Cl was decomposed into HCl or Cl_2 and absorbed into H_2O_2. The solution was then pumped into a suppressor-type ion chromatograph (HIC-20ASP; Shimadzu). Anion-mixed standard solution (F^-, Cl^-, NO^{2-}, Br^-, NO^{3-}, PO_4^{3-}, and SO_4^{2-} in water) from Kanto Chemical Co. Inc. was used as an external standard for the quantification. Five-point standard calibration curve was prepared at Cl concentrations of 0, 0.5, 2, 5, and 10 mg/L. Detailed information on the analytical conditions and typical chromatograms are provided in Table S4 and Figure S8, respectively.

The concentrations of insoluble Cl (μg Cl/g), $C_{\text{insoluble Cl}}$, were determined by eq 1

$$C_{\text{insoluble Cl}}(\mu\text{g Cl/g}) = C_{\text{Cl in residue}}(\mu\text{g Cl/g residual sample}) \times W_{\text{after washing}}(\text{g}) / W_{\text{before washing}}(\text{g}) \quad (1)$$

where $C_{\text{Cl in residue}}$ is the concentration of Cl in the residue (μg Cl/g residual sample), $W_{\text{after washing}}$ is the weight of dried residue after washing (g), and $W_{\text{before washing}}$ is the weight of the original sample (g).

Cl K-Edge XANES Measurement and Analysis. Cl K-edge XANES, including 18 sample spectra (Figure 2B) and 26 standard spectra (Figures 2A and/or S2), were measured between 2810 and 2860 eV at beamline BL-11B or BL-9A of the Photon Factory in Tsukuba, Japan. Sample spectra were collected at BL-11B or BL-9A using the fluorescence yield method. Standard spectra of PVC and inorganic Cl group except for chloride ion (NaCl solution) were collected at BL-11B using the electron yield method. Chloride ion (NaCl solution) was measured at BL-9A using the fluorescence yield method. Standard spectra of aromatic-Cl group were collected at BL-9A using the electron yield method. Samples were applied to carbon tape and irradiated with soft X-rays. The detailed procedure has been reported elsewhere.[31] Since we have already checked the good reproducibility of Cl K-edge XANES using the same beam lines previously, we measured once or used single scan here.

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Cl K-edge XANES spectra correspond to the electronic transitions from the Cl 1s core orbitals to vacant atomic and molecular orbitals of 3p character.[8,10] Therefore, the peak positions and shapes of Cl K-edge XANES vary according to the bonding state of Cl. This variation allows us to get the proportions of aromatic-Cl, aliphatic-Cl, and inorganic Cl using LCF analysis.

Data were processed using Athena analytical software (version 0.9.25).[77] All XANES spectra were calibrated against the intense absorption feature of solid KCl at 2822.8 eV. We normalized in the proper range between 2810 and 2819 eV for preedge and in the proper range between 2830 and 2860 eV for postedge to have their edge jump 1.0.

Before LCF analysis, we first conducted principal component analysis to determine the number of components necessary to explain the variation within the data set.[78] We conducted the analysis on the series of 18 sample spectra using Athena analytical software. Then, target transformation[78] was applied to identify the probable Cl species and chose 22 probable reference spectra out of 26 reference spectra ($PbCl_2$, $CuCl_2$, $CuCl_2{\cdot}2H_2O$, and $FeCl_3$ were removed).

For speciation, LCF of sample spectra was conducted in the range of 2815−2830 eV with the spectra of 22 standard materials (other than $PbCl_2$, $CuCl_2$, $CuCl_2{\cdot}2H_2O$, and $FeCl_3$ in Figure S2). Weights of standard spectra were forced to sum to 1 and restricted from 0 to 1. E_0 were fixed to 2820 eV. The residual value, $R = \sum(X_m - X_c)^2/\sum X_m^2$, where X_m is the measured XANES spectrum and X_c is the calculated XANES spectrum, was used to evaluate the LCF of the sample spectra. First, we used up to five possible standard spectra and fit all combinations to make the least R value. Then, we removed the standard spectra whose contribution weight was below 10% because the uncertainties of LCF analysis were up to 10% (see Supporting Information for the preliminary analysis to decide 10%). After that, we added or removed standard spectra one by one to check whether each standard spectrum should be included as end members or not. If R value changed by 10% or more, the standard spectrum should be included as end members.[79] We repeated these processes to check all of the standard spectra. The final contribution weights of standard materials, their uncertainties, and R values are described in Table S5.

Calculation of Identified Cl. Concentrations of identified Cl, sum Cl concentration from all identified individual compounds, were calculated from certified, reference, or reported concentrations using eq 2

$$C_{\text{identified Cl}} = \sum [N_i \times (35.453/\text{MW}_i) \times C_i] \quad (2)$$

where C_i is the concentration of compound i (ng/g), N_i is the number of Cl atoms bonded to aromatic or aliphatic organic carbon in compound i, 35.453 is the atomic weight of Cl, and MW_i is the molecular weight of compound i. We used certified or reported concentrations of individual OCs for the concentration of compound i (see the Supporting Information for details). We calculated identified aromatic-Cl and identified aliphatic-Cl separately. In this calculation, Cl atoms bonded to cyclic carbon in some pesticides are regarded as aromatic-Cl because the Cl K-edge XANES spectral peak is reported to be at 2821.2 eV, which overlaps with the peak for aromatic Cl compounds.[10]

Measurement of Total Organic Carbon. For inorganic carbon removal, 5 mL of 2 M HCl was added to 0.3 g of original sample and gently shaken. After being left to stand for 6 h, the sample was centrifuged. The residue was dried and analyzed using a TOC analyzer (TOC-VCSH/SSM-5000A; Shimadzu) at 900 °C, under conditions of 99.9% O_2 gas (150 mL/min) and 0.3 MPa (3 kg/cm^2) G pressure. D-(+) Glucose (TOC 40%) was used as a standard substance. We used information of mass fraction values of organic carbon (10.5%) for the urban PM sample, NIST SRM 1648a.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b00049.

Preliminary experiments and analysis (Tables S1−S5); relationship between organic, inorganic, extractable, and insoluble chlorine (Figure S1); normalized XANES spectra of 26 standard materials used for LCF fitting (Figure S2); quantitative speciation before and after washing (Figure S3); flow diagram for the procedure used to fractionate total chlorine (TCl) and insoluble chlorine (Figure S4); relative concentrations of chlorine in the residues after washing (Figure S5); relative concentrations of Cl in the residues of fly ash and natural forest soil (Figure S6); relative concentrations of Cl in the residues (Figure S7); and chromatograms of standard solution and house dust (Figure S8) (PDF)

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Notes

The authors declare no competing financial interest.

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